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Abstract

Isothermal crystallization of a high molecular weight PEO (M_w= 4,000,000) has been investigated using photoDSC. Combining light irradiation, heating and DSC analysis, photoDSC demonstrates a good capability to follow the in situ photo and thermo ageing of semi-crystalline polymers. Isothermal crystallization of PEO has been performed at 55°C. After ageing at different temperatures ranging from 0 to 90°C and for various periods of time, the kinetics of this crystallization has been found following Avrami theory. Avrami exponent, n, was found between 0.9 and 1.4 evidencing a one-dimension growth process. It was also found that the isothermal crystallization rate (i.e. reciprocal crystallization half-time) was exposure time, ageing temperature and light intensity dependent which makes this kinetic parameter a good indicator to follow and to compare the degradation of the semi-crystalline polymers.

Key Words

PhotoDSC, PEO, isothermal crystallization, Avrami, in situ ageing, polymers.

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Introduction

The crystallization processes of semi-crystalline polymers are very sensitive to the thermal and mechanical "history" of the material. Ability of the polymer to crystallize (also called "crystallizability") is strongly dependent on the capability of its macromolecular chains to move and to adopt the right conformation. Photo-oxydation in out door or in accelerated condition as well as thermo-oxydation lead to large modification in the polymeric architecture. In this paper, the crystallizability was used as a degradation progress indicator. PhotoDSC, combining in a single device irradiation, heating and DSC analysis, was considered for measuring the rate of isothermal crystallization of poly (ethylene oxide) (PEO) irradiated and heated at various temperatures. Isothermal crystallization of semi-crystalline polymers has been widely studied [1-4]. Avrami analysis is the most popular and easiest methodology to reach relevant parameters to characterize the crystallization kinetics of these materials. A well-documented paper, comparing Avrami, Tobin, Malkin and Urbanovici-Segal macrokinetic models has been published by Supaphol [5]. According to Supaphol's work, Avrami model is still one of the best with Urbanovici-Segal one, we consequently considered Avrami theory since it is easy and reliable enough to reach our specific goal.

PEO is a semi-crystalline water-soluble polymer [6,7], with a crystallinity which is very sensitive to the thermal history of the samples, making this property interesting as an indicator of degradation. Because it is a biodegradable and biocompatible polymer, PEO is a good candidate for environmental and medical applications [8, 9, 10]. The mechanisms of thermo and photooxidation of PEO have already been investigated [11, 12] on the basis of IR identifications of the oxidation products.

Experimental section

Materials

Poly(ethylene oxide) with high molecular weight (M_w= 4,000,000) was used. It was supplied by Scientific Polymer Products and used without further purification. The polymer is under white powder form. PEO is a semi-crystalline polymer. It exhibits a melting endotherm centred around 57°C (T_m) and a crystallization peak showing a large supercooling phenomenon starting at 35°C.

Methods

The photoDSC device used in this study was already described in (13,14). It combines light irradiation and DSC analysis applied to a single sample using a Hamamatsu light generator equipped with a Lightningcure200 source (Xe/Hg, "medium pressure") and a Metter Toledo DSC 822^e apparatus. The DSC device was equipped with an Intracooler unit providing a cooling rate up to 50 °C.min^{-1}. Temperature and energy calibration was performed using an indium standard sample (T_m = 156.6°C and ΔH = 28.5 J.g^{-1}). Aluminium DSC crucibles with 40 µL in capacity were used. No cover was used in order to bring the light beam directly onto the sample. All DSC runs were carried out under air atmosphere flow with 20 mL min^{-1} as flow rate.

Figure 1 should around be here

Figure 1 shows the details of the experimental measurements. In order to evaluate the specific contribution of heating and irradiation during the ageing of polymer, two series of runs have been performed. The first one was carried out with a simple heating in darkness whereas the second run was carried out under irradiation. For photo-ageing experiments (Figure 1 a), the sample was heated to the chosen ageing temperature ($T_a \leq$ 60°C, for instance T_a = 35°C in Figure 1a) for two minutes in darkness followed by a selected irradiation time increment (t_i). After t_i irradiation time, light was turned off and the sample heated at 10°C.min^{-1} up to 80°C. After 2 minutes at 80°C, the melting was completed and a fast cooling (20°C.min^{-1}) was imposed to the chosen isothermal crystallization temperature (T_c = 55°C). Sample was then maintained at this temperature for 90 minutes in order to assure complete isothermal crystallization. Immediately after isothermal crystallization, the sample temperature was changed to T_a and a new cycle was initiated. In order to check whether or not premature crystallization occurs during the fast cooling, a separate experiment was performed. In this experiment, instead of waiting at T_c for sample to completely crystallize, a heating scan was immediately performed as soon the thermal stabilisation was reached. No melting peak was observed in this subsequent heating scan. This observation was also supported by the absence of crystallization peak during the cooling segment. Four photo-ageing temperatures were investigated: 0, 15, 35 and 60°C. For T_a>60°C, changes induced by photo ageing were too fast and no isothermal crystallization peak was observed even after very short time increment.

For thermal oxidation experiments, the temperature program is shown in figure 1b (T_a=80°C). Except for the lighting step, the same experimental procedure was followed. Four ageing

temperatures were selected: 60, 75, 80 and 90°C. The crystallization after thermal ageing at temperatures lower than 60°C was found too slow to be carried out in a reasonable experimental time.

Results

Figures 2a and 3a show typical series of DSC exotherms of isothermal crystallization of PEO photo and thermo-aged at 15 and 80°C respectively for various exposure times. The isothermal crystallization temperature was 55°C in each case. Upon increasing irradiation or cure time, the isothermal crystallization peaks become wider and their top temperature shifts towards the longer times. In figures 2b and 3b are represented the integral curves from the DSC exotherms of isothermal crystallization whereas in Figures 2c and 3c are plotted two representations of the relative crystallinity, $\alpha(t)$, as a function of crystallization time, t. The relative crystallinity can be defined as follows:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{\infty}} \qquad \text{(Eq. 1)}$$

$\Delta H(t)$ is the enthalpy of isothermal crystallization at t and ΔH_{∞} its value after complete crystallization.

A relevant kinetic characterisation, obtained by derivation from the relative crystallinity plots, is the crystallization half time ($t_{0.5}$). This time corresponds to the time necessary for the polymer to reach 50 % of its maximum crystallinity. The reciprocal value of $t_{0.5}$ is assumed to be equal to the experimental rate (G_{exp}) of the isothermal crystallization. Tables 1 and 2 summarize the G_{exp} values as derived from Figures 2c and 3c. It can be noted that the crystallization rate decreases continuously when the irradiation or the curing time increases.

Figure 2 should around be here

Figure 3 should be around here

t /s	0	30	60	90	120	150	180
$t_{0.5exp}$ /s	105.3	137.3	159.8	179.8	207.8	262.3	345.6
G_{exp} x10^3 /s^{-1}	9.5	7.3	6.3	5.6	4.8	3.8	2.9

Table 1: Crystallization half-times ($t_{0.5exp}$) and experimental crystallization rate (G_{exp}) for photo-oxidation of PEO at 15 °C. Tc was 55°C.

t/s	0	120	240	360	480	600	720	840	960	1080	1200
$t_{0.5exp}$ /s	101.3	163.5	196.4	211.3	223.1	234.2	242.8	249.5	254.9	260.7	266.2
G_{exp} x10^3 /s^{-1}	9.9	6.1	5.1	4.7	4.5	4.2	4.1	4.0	3.9	3.8	3.7

Table 2: Crystallization half-times ($t_{0.5exp}$) and experimental crystallization rate (G_{exp}) for thermo-oxidation at 75°C.

More kinetic information can be obtained from these experimental data by application of Avrami formalism (15-17). Fundamental Avrami equation can be expressed as:

$$\alpha(t) = 1 - \exp(-k_a t^n) \qquad \text{(Eq. 2)}$$

where k_a is Avrami rate constant and n Avrami exponent.

The value of Avrami exponent is assumed ranging from 1 to 4 and is related to the geometric characteristics of nuclei: n=1 being ascribed to a rod, 2 to pellets and 3 or 4 to three-dimensional structure.

To calculate k_a and n, a log-log graphic representation is classically used:

$$\log\left(-\ln\left(1-\alpha(t)\right)\right) = \log\left(k_a\right) + n\log(t) \qquad \text{(Eq. 3)}$$

Thus, if the experimental data obey to Avrami theory, the plot of log(-ln(1-α(t))) as a function of log(t) should be linear yielding log(k_a) as intercept and n as slop.

Figure 2d and 3d show Avrami plots related to photo- and thermo-aged PEO at 15 and 80°C respectively. These plots were drawn for α(t) ranging between 0.1 and 0.56. To investigate whether or not the crystallization of PEO follows Avrami model's, the half-time crystallization values were calculated from the knowledge of k_a and n.

In fact, it can be written:

$$G_{cal} = \frac{1}{t_{0.5cal}} = \frac{1}{(\frac{\ln 2}{k_a})^{\frac{1}{n}}} \qquad \text{(Eq. 4)}$$

where $t_{0.5cal}$ is the calculated half-time crystallization and G_{cal} the calculated crystallization rate.

In Tables 3 and 4 are given the derived k_a, n and G_{cal} for two selected conditions

t /s	0	30	60	90	120	150	180	210
n	0.98	1.06	1.18	1.30	1.40	1.47	1.49	1.48
$\log(k_a)$	-2.14	-2.41	-2.76	-3.09	-3.43	-3.74	-3.98	-4.16
G_{cal} x10^3 /s^{-1}	9.5	7.5	6.2	5.8	4.6	3.7	2.7	1.9

Table 3: Kinetic parameters (k_a and n) and the corresponding calculated crystallization rate (G_{cal}) for photo-oxidation at 15°C.

t/s	0	120	240	360	480	600	720	840	960	1080	1200
n	0.98	1.04	1.09	1.19	1.24	1.24	1.26	1.28	1.32	1.32	1.33
$\log(k_a)$	-2.14	-2.46	-2.64	-2.92	-3.06	-3.09	-3.17	-3.23	-3.34	-3.35	-3.39
G_{cal} x10^3 /s^{-1}	9.9	6.1	5.1	4.7	4.5	4.2	4.1	4.0	3.9	3.8	3.7

Table 4: Kinetic parameters (k_a and n) and the corresponding calculated crystallization rate (G_{cal}) for thermo-oxidation at 75 °C.

Discussion

The same analytical procedure, described above, has been applied to the experimental data collected from the photoageing at 0, 15, 35 and 60°C and the thermoageing at 60, 75, 80 and 90°C of PEO. Figure 4 illustrates the comparison between the isothermal crystallization rate as calculated from Avrami parameters (G_{cal}, empty symbols) and the same kinetic parameter as directly derived from the experimental relative crystallinity data (G_{exp}, filled symbols). The good agreement observed between the two series of data reveals that the crystallization kinetics of aged PEO follows the Avrami model. It is, however, worth mentioning that the

selected procedure, in this work, is not the classical one used in Avrami analysis. Classically, it is performed by varying the selected isothermal crystallization temperature (T_c). T_c is chosen in the range in which polymers can crystallize (i.e. $T_g<T_c<T_0$, with T_g the glass transition and T_0 the equilibrium melting temperature). When the melted semi-crystalline polymer is cooled down and maintained at T_c, it crystallizes with a crystallization rate (G) depending on its degree of supercooling (i.e. $\Delta T= T_0-Tc$). It is known that G decreases when T_c increases. In this work, the isothermal crystallization temperature was kept constant and the same for all experiments whereas the time exposure changes by successive time increments.

Figure 4 should be around here

Figure 5 should be around here

Figure 4 shows that the crystallization rate decreases continuously as a function of exposure time (irradiation or curing time) at each ageing temperature. The melting temperature (T_0) of PEO is 57°C and its glass transition temperature (T_g) is -60°C. The chosen isothermal temperature (T_c) was 55°C that corresponds to a very low supercooling. So, as stated in reference [5], it can be assumed that the global kinetics of crystallization is controlled by the nucleation step.

Whatever the ageing temperature for both photo- and thermo-ageing, Avrami exponent, *n*, was found ranging between 0.98 and 1.4. The crystallization seems to proceed with a one-dimension nucleation morphology. Beside, the decrease of crystallization rate is accelerated when the ageing temperature increases. As can be seen in Figure 5, comparing the decrease of G due to the photo-ageing or to the thermo-ageing at the same temperature (60°C), the light exposure causes also a drastic and fast fall in the crystallization rate. This observed sensitivity of the crystallization rate to irradiation and heating confirms our previous results [14] obtained by a non-isothermal crystallization procedure. During the step of irradiation or heating (at T_a) PEO underwent various oxidation reactions. Chain scissions and cross linking are the two more important consequences of these reactions. Cross linking, by the induced drastic limitation of the degree of freedom of the macromolecular chains, could provoke the decrease of the ability of the polymer to crystallize. Also, the chain scissions, by the disordering of the macromolecular segments, prevent the polymer to adopt the right conformation to crystallize. Various evidences, provided by rheology, IR spectroscopy and

Atomic Force Microscopy (AFM), have been published showing that PEO undergoes a chain scission phenomenon rather than cross linking.

The mechanism given in reference [11] recalls that formates are formed with chain scission whereas the formation of esters does not involve the cleavage of the macromolecular backbone. PhotoDSC, used in this isothermal crystallization mode, gives a reliable and simple way to follow the ageing of semi-crystalline polymers allowing a complete control of light intensity, temperature and atmosphere composition.

Conclusion

PhotoDSC, combining irradiation, heating and DSC analysis, has been used to follow the photo- and thermo-ageing of a high molecular weight PEO. DSC analysis consisted in the recording of the isothermal crystallization exotherms. It was found that the kinetics of the crystallization of the aged PEO follow the Avrami theory and that the nucleation proceeds by one-dimension morphology ($0.9<n<1.4$). The isothermal crystallization rate (G) decreases continuously when the exposure time (irradiation or curing time) increases. G decreases also when the ageing temperature increases. When, at the given temperature, PEO is irradiated, the decrease of G is accelerated. The crystallisation rate can be then chosen as a relevant experimental parameter to follow and compare the ageing of semi-crystalline polymers.

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